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Blue-green and red luminescence from non-polar ZnO:Pb films

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ABSTRACT

Pure zinc oxide (ZnO) and lead (Pb) doped zinc oxide (ZnO:Pb) films with different Pb doping concentrations were deposited on glass substrate by using radio frequency reactive magnetron sputtering technique. X-ray diffraction spectroscopy measurements showed that all samples with the (1 0 0) preferential orientation were growth of the non-polar. The results of X-ray photoelectron spectroscopy analysis suggested that the Pb ions were successfully doped into lattice of ZnO and the valence of Pb in the ZnO films was a mixed state of +2 and +4. Optical band gaps of the ZnO:Pb were 3.24, 2.92, 2.86 and 2.74 eV with the increase of Pb doping concentration, it could attribute this red shift phenomenon to the decrease of carrier concentration. Photoluminescence measurements showed that a broad emission band including the two blue emission peaks are about at 437 nm and 470 nm, one green and red emission peaks are about at 510 nm and 710 nm, which may compound white light. Moreover, growth of non-polar ZnO enhanced enormously the luminous efficiency of photoluminescence in our experiment. The current–voltage measurements between two surface electrodes showed the increase in resistance with increase of Pb doping concentration.

1. Introduction

In recent years, many attention have focused on light emitting diode (LED) based white light sources for lighting purposes. Among various semiconductor nanomaterials, ZnO films have attracted great scientific and technological interest owing to its direct wide band gap (3.37 eV), large exciton binding energy (60 meV).

As we known, many elements have been doped into ZnO films in order to adjust its properties in the recent years, such as Co, Ga and Ag [1–3]. Although, to the best of our knowledge, there are some literatures [4,5] that investigated the properties of ZnO:Pb nanowires, but the achieved properties from ZnO:Pb films are very excellent and unique. We have obtained full non-polar ZnO films by suitable Pb doping concentration that grew along the direction of the vertical (1 0 0) rather than the (0 0 2) direction [6,7], that is to say the films grow along the direction of the (1 0 0) and (1 1 0) in our experiment. The ZnO film with (0 0 2) preferred orientation is the polar film that generated internal electric field and reduces the luminous efficiency of the ZnO-based light emitting device. However, the non-polar ZnO film is able to eliminate the adverse effect of internal electric field. Meanwhile, the blue, green and red emission peaks appeared at same time in our non-polar ZnO films. The red, green and blue emission, the three primary colors of light, could compound white light. So the ZnO:Pb films were excellent candidate for possible luminescence applications.

In this paper, the influence of different Pb doping concentrations on the microstructure, optical and electrical properties of ZnO films are investigated via X-ray diffraction, X-ray photoelectron spectroscopy, UV/vis, fluorescence spectrophotometry, electrochemisty workstation and 4-point Probes Resistivity Measurement System, respectively.

2. Experiments

The ZnO:Pb films were deposited on glass substrates by using radio frequency (RF) reactive magnetron sputtering under different Pb doping concentration. In order to control the Pb doping concentration, the effective sputtering area ratios of Pb and Zn were varied 0%, 0.75%, 1.5% and 2.5% corresponding to samples (a), (b), (c) and (d), respectively. The Pb concentrations of ZnO:Pb films were 0, 1.17, 1.53, and 2.24 at.% corresponding to samples (a), (b), (c) and (d), respectively, which were determined by energy dispersive spectrometer (EDS, JSM-6701F). Argon and oxygen (purity 99.99%) were used as the sputtering and reactive gas. All the films were deposited with RF power of 100 W under pressure of 1.0 Pa for 1 h, the O_2:Ar ratio was 12:8 sccm. All films were annealed in vacuum at 500 °C for 1 h.

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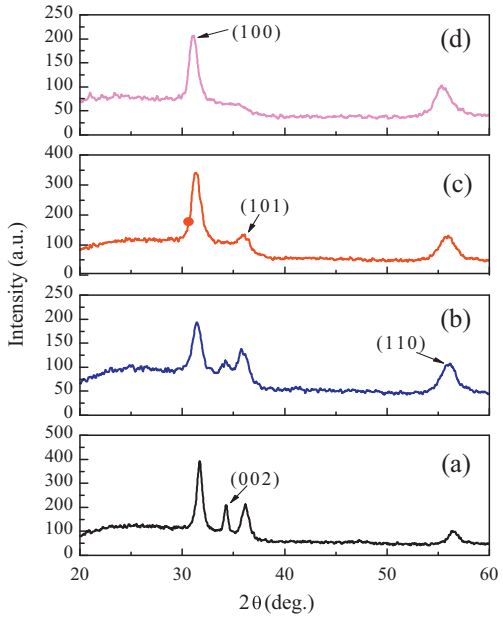

Fig. 1. XRD patterns of ZnO:Pb films with different Pb doping concentration: (a) 0%, (b) 1.17 at.%, (c) 1.53 at.% and (d) 2.24 at.%.

The microstructure, optical and electrical properties of ZnO films are investigated via X-ray diffraction (XRD) (D/Max-2400) using the Cu Kα radiation with λ = 0.15406 nm, X-ray photoelectron spectroscopy (XPS) (ESCA LAB 220-XL), Lambda 35UV/VIS, fluorescence spectrophotometry (PL) the excitation of Xe lamp (RF-5301, wavelength 360 nm), electrochemisty workstation (CHI660D) and 4-point Probes Resistivity Measurement System (RTS-8). All spectra were measured at room temperature in air.

3. Results and discussion

3.1. Structure properties

Fig. 1 shows the XRD patterns of ZnO:Pb films that were fabricated under different Pb doping concentration. It is observed from the figure that all films show dominant peak corresponding to the (1 0 0) direction of ZnO and other weak peaks corresponding to the (0 0 2), (1 0 1) and (1 1 0). All samples grew along to the non-polar direction and full growth of non-polar was obtained in the sample (d) (Fig. 1(d)). In order to further explain non-polar growth, the texture coefficient (TC) which can describe the preferential orientation is calculated by using the following expression [8]:

$$TC_{(hkl)} = \frac{I_{(hkl)}}{I_{(100)} + I_{(002)} + I_{(101)} + I_{(110)}} \quad (1)$$

where $TC_{(hkl)}$ is the texture coefficient of (hkl) plane, $I_{(hkl)}$ is the intensity of the diffraction peak. As can be seen in Fig. 2, the $TC_{(100)}$ decreases slightly at first and then increases sharply, meanwhile the $TC_{(110)}$ increases gradually with the increase of Pb doping concentration. The $TC_{(002)}$ decreases to zero in the end. This phenomenon further indicated that the increase of Pb doping concentration could promote the non-polar growth and inhibit the polar growth.

It was obvious that preferential orientation of ZnO films were strongly affected by Pb doping. The most important is that Pb doping have successfully achieved the transform of preferential orientation of ZnO films from blended growth to complete non-polar growth, which are able to eliminate the adverse effect of internal electric field that exist in the polar ZnO films and improve luminous efficiency. Waltereit et al. [9] have reported the luminous efficiency of non-polar film (GaN-based LED) has significantly improved. ZnO

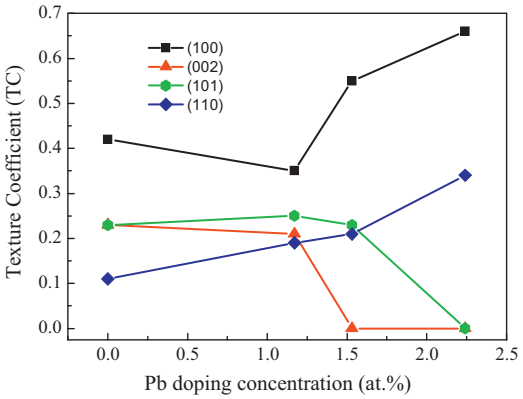

Fig. 2. Variation of $TC_{(100)}$, $TC_{(002)}$, $TC_{(101)}$ and $TC_{(110)}$ of ZnO:Pb films with increase of Pb doping concentration.

films generally showed (0 0 2) preferred orientation that perpendicular to the substrate due to the lower surface free energy of (0 0 2) plane [5]. But in our experiment (1 0 0) plane had the lowest surface free energy because of all samples have exhibited (1 0 0) preferred orientation. Therefore, Pb doping increases the surface free energy of (0 0 2) plane, which leads to the (0 0 2) diffraction peaks vanished, and decreases the surface free energy of (1 0 0) plane.

Moreover, the diffraction angles of (1 0 0) diffraction peaks are 31.70°, 31.42°, 31.32° and 31.06° corresponding to the samples of (a), (b), (c) and (d), respectively. It was obvious that the diffraction angles of ZnO:Pb films (1 0 0) diffraction peaks shifted to lower angle with the increment of the Pb doping concentration. Fig. 3 was an enlarged view of (1 0 0) diffraction peaks and obviously showed the change of diffraction angles of (1 0 0) diffraction peaks. Ma et al. [10] reported that when Cu^{+} ions (radius is 0.096 nm) substitute Zn^{2+} ions (radius is 0.074 nm) at their lattice sites, this resulted in the increase of the crystalline plane distance, which would lead to the decrease of the diffraction angle compared with pure ZnO film. That is consistent with our results. The valence of Pb could be

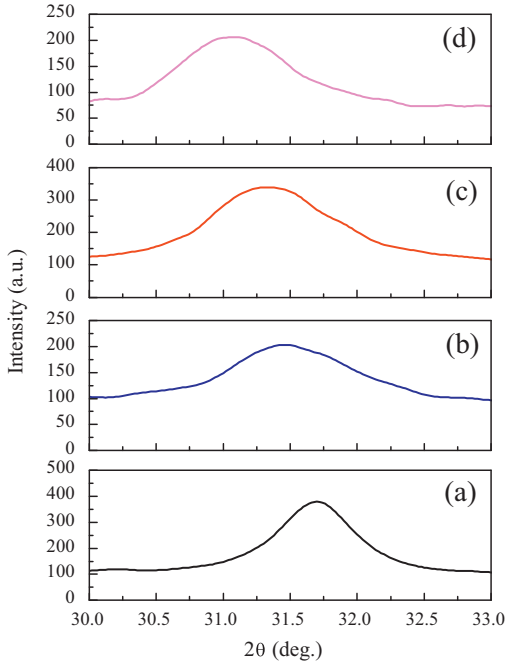

Fig. 3. Enlarged figures of (1 0 0) diffraction peaks with different Pb doping concentration: (a) 0%, (b) 1.17 at.%, (c) 1.53 at.% and (d) 2.24 at.%.